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(Unclassified Title)

QUARTERLY PROGRESS REPORT,
INORGANIC HALOGEN OXIDIZERS

(29 August 1965 through 28 November 1965)

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

Contract Nonr 4428(00)

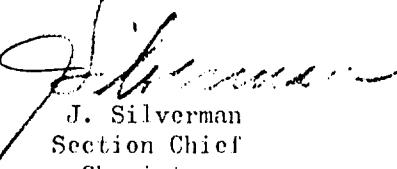
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FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency through the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Contract Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 August 1965 through 28 November 1965. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, responsible for coordinating this report; Dr. C. J. Schack; and Dr. C. B. Lindahl.

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ABSTRACT

The fluorination of KF and CsF complexes of Cl_2O has yielded ClF_3O . Thermal dissociation of KClF_4O occurred below ambient temperature while heating was required to dissociate CsClF_4O .

Oxychlorine trifluoride has also been prepared from chlorine nitrate in a 95+ percent yield by fluorination of the complex CsClFONO_2 . The reaction was independent of the presence of N_2O_4 . Glow discharge experiments at -196 C with solid Cl_2O and activated fluorine gas have resulted in small quantities of ClF_3O , but ClF_5 and FClO_2 were the major products.

The hydrolysis of ClF_5 with potassium fluoride dihydrate and excess potassium fluoride was carried out in a flow system. No ClF_3O was obtained.

The ratio of CsF to ClF_3O in this complex has been determined to be 1.15 when using excess ClF_3O . Experiments with excess CsF also demonstrated an incomplete attainment of stoichiometry indicating unfavorable kinetics for the reaction. Reversible dissociation of the complex occurs below 150 C.

The basic behavior of ClF_3O was shown by its reaction with PF_5 and SiF_4 to form 1:1 and 2:1 complexes respectively. The reaction of ClF_3O with FNO to form a reversible

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complex demonstrated its acidic properties. Oxychlorine trifluoride was displaced from its CsF complex by ClF₃ and from its PF₅ complex with FNO. Vapor pressure/temperature equations for the ClF₃O·FNO and (ClF₃O)₂SiF₄ complexes were obtained.

The synthesis of ClF₅O was attempted by the fluorination of CsClF₄O and by the reaction of KrF₂ with ClF₃O. Oxychlorine trifluoride was recovered in each case. Partial fluorination of Cl₂O·CsF was investigated as a route to chlorosyl fluoride and gave only traces of an unidentified substance thought to be FCLO. The reduction of ClF₃O as a possible route to FCLO was tried with the reducing agents Cl₂O, SO₂, Br₂, and BrF₃.

The complex of Br₂O and CsF has been fluorinated in hopes of forming BrF₃O or BrF₅O.

The fluorination of N₂O in the presence of CsF was attempted as a possible path to new F, N, O compounds. Neither complex formation nor reaction with fluorine was noted.

In an effort to demonstrate the existence of mercury hypochlorite as a possible intermediate, reaction products of Cl₂ and HgO, as well as Cl₂O and HgCl₂, were studied. No direct or reproducible evidence supporting mercury hypochlorite structures was obtained.

(Confidential Abstract)

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INTRODUCTION

During the present quarter, the studies revolving around oxychlorine trifluoride were expanded. In addition to studying the chemistry of its formation and intermediates involved, some attention was given to the chemistry of ClF_3O itself.

The chemistry of ClF_3O thus far is being pursued in two ways. The most important is the potential of ClF_3O as an intermediate in both fluorinations and reductions. Accordingly, the results of Rocketdyne studies in this connection will be presented in detail. Acid-base equilibria involving ClF_3O are also of interest. Some new species derived from ClF_3O in this context have been partially characterized.

Because preliminary characterization of ClF_3O is complete, more attention has been devoted to seeking other oxyhalogen fluorides. In this vein, fluorination studies of Br_2O were resumed.

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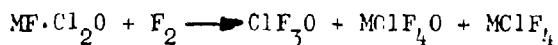
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TECHNICAL DISCUSSION

FLOROX STUDIES*

Synthesis of Oxychlorine Trifluoride From
Cl₂O-Alkali Metal Fluoride Complexes

The fluorination of Cl₂O, complexed with alkali metal fluorides, has continued to provide the primary route to ClF₃O:



When CsF was used, part of the ClF₃O was evolved by warming to room temperature. Additional ClF₃O as well as ClF₃ was obtained by thermal dissociation of the residual solids.

In contrast, no additional ClF₃O was evolved when the products from the fluorination of KF·Cl₂O were heated above ambient temperature. The total yield was obtained by simply warming to ambient temperature. When the other product, ClF₃, was driven off by heating, the potassium fluoride could be reused with no loss of efficiency, similar to the satisfactory reuse of CsF in these fluorination reactions.

The ease of workup from KF-containing fluorinations suggests that KC1F₄O is appreciably dissociated at ambient temperature while CsClF₄O requires considerable heating for complete dissociation. Moreover, a simple technique for the separation of ClF₃ from ClF₃O may be possible using KF. It was found that CsF was unsuitable in this regard.

*Unclassified designation for ClF₃O

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While a high conversion of Cl_2O to ClF_3O was not achieved using potassium fluoride, reasonably good yields have been obtained during initial experiments. At first, a yield of 9 percent based on Cl_2O was achieved. Subsequent runs in the same container gave yields of 44 percent based on Cl_2O and, following KF regeneration, 43 percent based on KF in a run with excess Cl_2O .

Electric Discharge Fluorination of Solid Cl_2O

Earlier in this program, the use of electric-discharge-activated fluorine was tried in reactions with solid Cl_2O to achieve the synthesis of ClF_3O . At that time (Ref. 1), it was observed that some ClF_5 was found but no ClF_3O . This reaction was re-examined using recirculated fluorine in a closed-loop system at low pressures rather than the simple flow-through method. As expected, a much more efficient fluorination was achieved. The yield of ClF_5 was approximately 45 percent (based on 2ClF_5 for each Cl_2O). In addition, small quantities of ClF_3O were found along with some ClF_3 and much FClO_2 .

Therefore, with the incorporation of this improved technique, the general utility of the electric discharge fluorination process has been improved and made more efficient. Also, it is expected that this activated gas solid reaction method might now be employed to demonstrate the synthesis of other highly fluorinated species, in particular ClF_5O .



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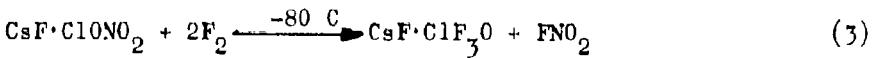
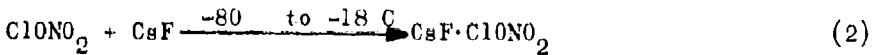
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Synthesis of Oxychlorine Trifluoride from ClONO₂

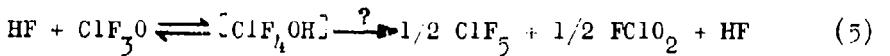
Two additional syntheses of ClF₃O via ClNO₃, CsF, and F₂ have been conducted in the same manner as reported previously (Ref. 2). The first, employing previously used CsF, gave no product. The second, utilizing fresh CsF, gave a 95+ percent yield of ClF₃O. In this reaction, it was noted that some of the ClF₃O was obtained as part of the volatile species, whereas in the past, it was observed only on pyrolysis of the solids left after completion of the fluorination. Nitryl fluoride was the only other major product obtained, thus confirming the postulated reaction sequence:



It is also noteworthy that the ClNO₃ employed in this high-yield ClF₃O synthesis was contaminated with NO₂. The NO₂ impurity had no detrimental effect other than to consume fluorine in being converted to FNNO₂.

Hydrolysis of ClF₅ With Potassium Fluoride Hydrate

Previous attempts (Ref. 3) to produce ClF₃O by hydrolysis of ClF₅ have unsuccessfully utilized metal fluoride hydrates. Because HF is a product of such a reaction it may have been detrimental to the formation of ClF₃O:



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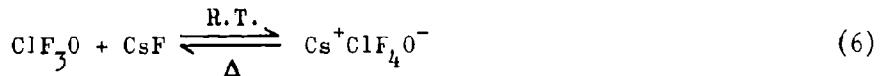
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Therefore, the reaction was repeated using ClF_5 , $\text{KF} \cdot 2\text{H}_2\text{O}$, and a large excess of KF so that the HF formed would be tied up as KHF_2 . Chlorine pentafluoride at 60-mm pressure was passed through a 10:1 powdered mixture of KF and $\text{KF} \cdot 2\text{H}_2\text{O}$ in a Kel-F flow reactor. The first reaction yielded FClO_3 , FClO_2 , Cl_2 , and noncondensibles. The second reaction gave mostly FClO_2 and small amounts of FClO_3 .

The third reaction gave FClO_2 and unreacted ClF_5 . The reactivity of ClF_3O , if formed, is apparently greater with metal fluoride hydrates than is ClF_5 .

Studies of the Cesium Oxychlorine Tetrafluoride Complex

The reversible nature of the $\text{CsF}-\text{ClF}_3\text{O}$ system has been reported (Ref. 2).



However, no information regarding the actual stoichiometry was obtained because all the earlier experiments were conducted with a large molar excess of CsF. When the complex formation was carried out using measured amounts of CsF and ClF_3O , and with an excess of the latter, an experimental composition $\text{CsF}_{1.15} \cdot \text{ClF}_3\text{O}$ was obtained. This composition is reasonably close to a 1:1 complex, especially considering the problem of solid/liquid contact.

The formation of cesium oxychlorine tetrafluoride was also examined using excess CsF rather than excess ClF_3O . After 3 days at ambient temperature, 83 percent of the ClF_3O was complexed and after 3 weeks at -16°C, 96 ± 3 percent of the ClF_3O was complexed. The failure of all the ClF_3O to be

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complexed is attributed to poor gas/solid contact after all the liquid ClF_3O has reacted because the $\text{Cs}^+\text{ClF}_4^-$ complex has a negligible vapor pressure of ClF_3O even at room temperature.

Because cesium oxychlorine tetrafluoride has potential utility as an intermediate in the synthesis of chlorosyl fluoride or oxychlorine pentafluoride, its thermal stability is of interest. Available data indicate that ClF_3O can be completely liberated from the cesium fluoride complex by pumping for several hours at 150°C. However, the nature of the complex giving rise to ClF_3O in this reaction was not accurately known because it was the result of the fluorination of the $\text{Cl}_2\text{O}\cdot\text{CsF}$ complex. An attempt was made to thermally dissociate any $\text{Cs}^+\text{ClF}_4^-$ present, leaving the byproduct ClF_3 in the complex form $\text{Cs}^+\text{ClF}_4^-$. The temperature required to liberate ClF_3O completely was well below that required to yield ClF_3 from $\text{Cs}^+\text{ClF}_4^-$ (Ref. 4). Yet, evolved ClF_3O was mixed with appreciable amounts of ClF_3 . This observation might be indicative of the retention of a fluorinated ClOCl moiety such as $\text{Cs}_2\text{ClF}_8\text{O}$. It is planned to check this possibility by heating a mixture of the independently prepared salts, $\text{Cs}^+\text{ClF}_4^-$ and $\text{Cs}^+\text{ClF}_4^-$, to see if the ClF_3O evolved in this case is also mixed with ClF_3 . If warranted, additional studies with X-ray powder diffraction will be carried out.

Reactivity of Oxychlorine Trifluorine With Monel

Previous experiments in Monel with F_2 showed 63-to 70-percent ClF_3O recovery at 200 to 236°C over 16-hour periods (Ref. 2). It was recently found that heating ClF_3O with CsF to 200°C in Monel for 3 days, converted all the ClF_3O to FClO_2 , ClF , and ClF_3 . These conflicting results may be the result of the formation of the F_2ClO radical which, in absence of fluorine, reacted with an incompletely passive Monel surface. It may be

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recalled that 16-hour experiments in stainless steel at 200 C gave only Cl₂ and O₂ (Ref. 2) in the absence of fluorine. It is possible that while F₂ClO is a hypothetical precursor to FC1O₂, ClF₃, and ClF in Monel, the same radical could give Cl₂ and O₂ with the more reactive stainless steel.

Oxychlorine Trifluoride Reactions With Acidic and Basic Fluorides

The ability of chlorine trifluoride to form complexes with both alkali metal fluorides and strong Lewis acids has been demonstrated with oxychlorine trifluoride as well. In addition to the previously reported reactions with boron trifluoride and arsenic pentafluoride (Ref. 2), ClF₃O reacted with both phosphorus pentafluoride and silicon tetrafluoride to form solid complexes. Phosphorus pentafluoride formed a colorless 1:1 complex with ClF₃O, which had less than 20 mm Hg pressure at ambient temperature. The solid could be moved by pumping but was presumably dissociated in the gas phase because no infrared spectral differences could be seen between the individual components and the vapor above the complex. A less stable complex was formed when ClF₃O and SiF₄ were mixed. When equimolar parts were brought to -80 C, one half of the SiF₄ reacted. Upon the addition of another equivalent portion of ClF₃O, the balance of the SiF₄ was complexed after temperature cycling. The vapor pressure of the 2:1 ClF₃O-SiF₄ mixture was measured at several temperatures between -80 and 14 C and the following vapor pressure/temperature equation was obtained:

$$\log_{10} p(\text{mm}) = 7.75 - 1545/T \quad (7)$$

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The enthalpy and entropy changes for the process $(\text{ClF}_3^0)_2 \cdot \text{SiF}_4$ (solid) \rightarrow 2ClF_3^0 (gas) + SiF_4 (gas) were calculated: $\Delta\tilde{H} \sim 22$ kcal, $\Delta\tilde{S} \sim 65$ e.u. An estimation of the enthalpy change in the process 2ClF_3^0 (l) + SiF_4 (s) \rightarrow $(\text{ClF}_3^0)_2 \cdot \text{SiF}_4$ (s) was made from the heats of vaporization and sublimation of ClF_3^0 and SiF_4 : $\Delta\tilde{H} \sim 2$ kcal. The complex may be written as either $(\text{ClF}_2^0)^+ \cdot (\text{ClF}_3^0)_2 \cdot \text{SiF}_4^-$ or $\text{ClF}_3^0 \rightarrow \text{SiF}_4 \rightarrow \text{OClF}_3$. Successive portions of the complex were removed at -23 C. Their infrared spectra showed a constant ratio of ClF_3^0 and SiF_4 absorbances indicating a 1.9 mole ratio.

The amphoteric behavior of ClF_3^0 was further demonstrated by its acidic reaction with nitrosyl fluoride. Apparently two complexes are formed, $\text{FN}0 \cdot \text{ClF}_3^0$ and $\text{FN}0 \cdot 2\text{ClF}_3^0$. The former complex was converted to the latter by pumping at -80 C. A vapor pressure/temperature curve was obtained for the $\text{FN}0 \cdot \text{ClF}_3^0$ complex from -80 to 0 C:

$$\log_{10} p(\text{mm}) = 8.47 - 1625/T \quad (8)$$

The heat of reaction for the combination of the liquids $\text{FN}0$ and ClF_3^0 to form the solid complex was calculated as about 5 kcal/mole of complex from the heats of vaporization of the liquids and the above equation.

The relatively high density, 1.9 g/cc, and heat of vaporization, 7.7 kcal/mole, of ClF_3^0 (Ref. 2) may be indicative of the existence of dimeric or bridged species in the liquid, e.g., $\text{ClF}_3^0-\overset{\delta+}{\text{O}}-\overset{\delta-}{\text{ClF}_3^0}$. The addition of fluoride might then result in the formation of the observed 2:1 complex $\text{N}0^+\text{ClF}_4^0-\overset{\delta-}{\text{O}}-\text{ClF}_3^0$.

When an equimolar amount of nitrosyl fluoride was added to the $\text{ClF}_3^0 \cdot \text{PF}_5$ complex at -80 C, ClF_3^0 was liberated.

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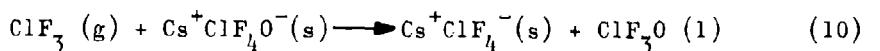
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An infrared spectrum of the products volatile at room temperature showed only ClF_3O indicating the following reaction:



Thus, as expected, ClF_3O is a weaker base to PF_5 than is FNO .

Oxychlorine trifluoride was also displaced from its complex with a fluoride base by using another acid. Addition of ClF_3 to CsClF_4O at ambient temperature liberated ClF_3O according to the equation:

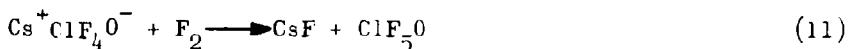


This confirms ClF_3 to be a stronger Lewis acid than ClF_3O toward CsF .

STUDIES LEADING TO NEW OXIDIZERS

Attempted Synthesis of Oxychlorine Pentafluoride

Oxychlorine trifluoride provides a potential intermediate for making both chlorosyl fluoride and oxychlorine pentafluoride. By analogy with the fluorination of $\text{Cs}^+ \text{ClF}_4^-$ to yield ClF_5 , the fluorination of the complex $\text{Cs}^+ \text{ClF}_4\text{O}^-$ would be expected to be a likely route to the new oxychlorine fluoride, ClF_5O .



Experiments with increasingly vigorous conditions of temperature and pressure have not resulted in ClF_5O or any other new compounds.

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Conditions imposed thus far have been 750 psi at 50 C, 850 psi at 100 C, and 1200 psi at 160 C. The ClF_3^0 was recovered essentially unchanged from the Monel reactor in each case.

Another possible route to ClF_5^0 is the direct fluorination of ClF_3^0 by KrF_2 (Ref. 5) at low temperatures. The possible utility of this reaction is indicated by the recent report of the preparation ClF_3^0 and KrF_2 (Ref. 6).



Good mixing of the reactants can only be achieved at temperatures above -65 C, the melting point of ClF_3^0 . In three reactions so far conducted, the materials were allowed to warm up together from that temperature to ambient temperature over several hours. No evidence was found, however, for the formation of any new materials. The KrF_2 underwent smooth thermal decomposition to Kr and F_2 , and some ClF_3 contaminant was partially converted to ClF_5 ; the ClF_3^0 was recovered quantitatively. Additional experiments are planned using shorter warming periods.

Reduction of Florox

The nonvolatile solid formed by low-temperature fluorination of the $\text{Cl}_2^0\text{-CsF}$ complex has been heated to yield ClF_3^0 , ClF_3 , and, on three occasions, ClF and traces of an unknown species. The unknown partially passed through a -156 C trap in a vacuum line. The two bands in the rock salt region were observed and are indicated in Fig. 1. Additional

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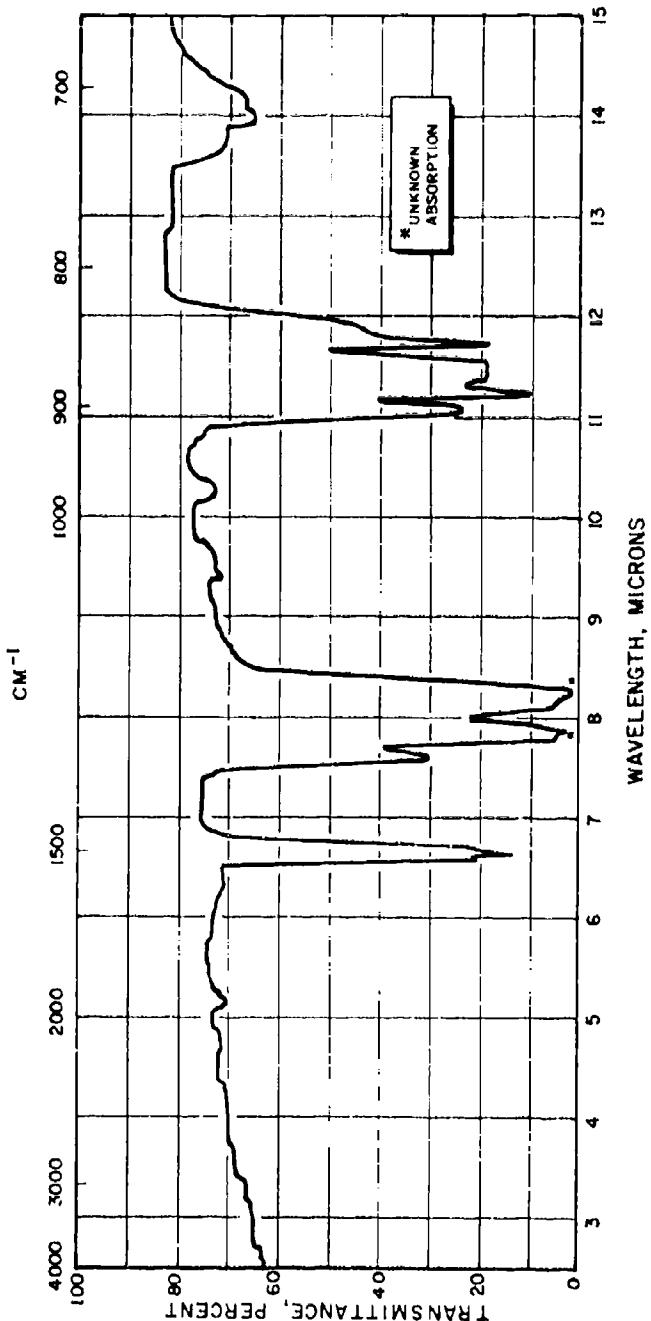


Figure 1. Pyrolysis of $\text{Cl}_2\text{O}-\text{CsF}$ Fluorination Products

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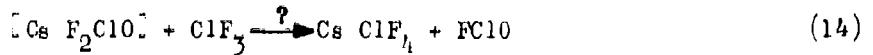
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bands were noted at 645, 630, 610 (a possible pqr), and possibly at 465 cm^{-1} . This unknown may be a new F, Cl, O compound and specifically may be FC1O. Mass spectrometric examination of a sample containing the unknown yielded no information. Three attempts to obtain the unknown by methathetical displacement by ClF_3 were unsuccessful:



Because only traces of the new material were found thus far, several new approaches have been utilized in the search for this elusive material. The concomitant presence (or absence) of ClF suggests synthesis of the unknown and ClF by a simultaneous degradation of $\text{Cs}^+\text{ClF}_4\text{O}^-$ and $\text{Cs}^+\text{ClF}_4^-$ complexes by incomplete fluorination of the $\text{Cl}_2\text{O}\text{-CsF}$ complex. Routine fluorinations of the $\text{Cl}_2\text{O}\text{-CsF}$ complex to ClF_3O and ClF_3 have utilized 3:1 $\text{F}_2:\text{Cl}_2\text{O}$ ratios. Intentional underfluorination to FC1O and ClF would require a $\text{F}_2:\text{Cl}_2\text{O}$ ratio of 1:1 according to the equation:



The incomplete fluorination at -80 °C yielded ClF_3O and much unreacted Cl_2O but only traces of the unknown. Apparently once the $\text{Cl}_2\text{O}\text{-CsF}$ complex was initially attacked by F_2 it was oxidized all the way to ClF_3O and ClF_3 .

Another approach to the synthesis of FC1O involves reaction of ClF_3O with appropriate reducing agents. With the reducing agent Cl_2O , FC1O could arise as an oxidation product as well as a reduction product:



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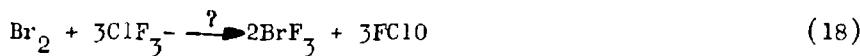
Thus, local excesses would present less of a problem. The experiment was run with equimolar amounts of reactants held at ambient temperature in Monel for 3 days. While all of the Cl_2O reacted, only half of the ClF_3O was used. The products were FClO_2 , smaller amounts of ClF , some chlorine, but no noncondensibles. Either FClO did not form or disproportionated according to the equation:



Milder reaction conditions, such as shorter reaction time, lower temperatures, and complexed reactants are indicated for future experiments. Further reaction or disproportionation of any FClO formed may be reduced by complex formation as well.

The reaction of sulfur dioxide with ClF_3O was carried out between -80 and 45°C in hopes of fluorinating SO_2 to SO_2F_2 and forming FClO . The major reaction products were SOF_2 and FClO_2 with minor amounts of SO_2F_2 . However, an overall decrease in the pressure of the system of 20 percent suggested some coupling or formation of a less volatile species. Infrared absorptions at 1485, 1240, 880, and 835 cm^{-1} indicated the presence of $\text{SF}_4(\text{SO}_3\text{F})_2$ (Ref. 7). Fluorination of this material by F_2 resulted in $\text{S}_2\text{O}_6\text{F}_2$ and SF_6 . No Cl-F absorptions above 660 cm^{-1} were seen.

The reaction of bromine trifluoride and oxychlorine trifluoride gave no new products. Bromine and oxychlorine trifluoride in a 1:3 mole ratio were reacted by slow warming from -80°C in anticipation of the following result:



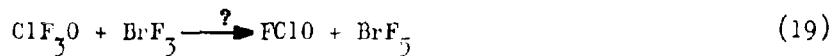
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Chlorine, chloryl fluoride, and some unreacted oxychlorine trifluoride were recovered. No evidence for BrF_3 or FClO was obtained. The failure to obtain FClO may have been caused by its reaction with bromine. Therefore, BrF_3 was tried as a reducing reagent:

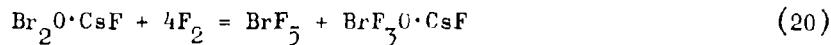


Bromine trifluoride and oxychlorine trifluoride did not react at room temperature. Higher temperatures may produce the desired reaction.

Attempted Synthesis of Oxybromine

Fluorides by Fluorination of Br_2O

On the basis of analogy with the Cl_2O system, it was expected that Br_2O represents a likely starting material for the preparation of the unknown BrF_3O and BrF_5O compounds. Because of the high melting point of Br_2O and thermal instability above the melting point, the required CsF complex was formed using Freon 11 as a solvent for Br_2O . The complex was obtained after removal of the solvent and has been utilized for several fluorination reactions now in progress at -50°C. One partially completed experiment has shown that nearly all the added fluorine was consumed. The only volatile products observed, however, were Br_2 and BrF_5 . No BrF_3 would be expected because it forms a stable complex with CsF. No new species were noted but this was not particularly discouraging because BrF_3O and possibly BrF_5O could be present as solid CsF complexes. Thermal dissociation of these solids is scheduled. The formation of BrF_5 in good yield was promising and may indicate the following reaction:



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Fluorination of N₂O

Success in the CsF-catalyzed low-temperature fluorination of carbon dioxide suggested that the isoelectronic molecule N₂O might also be fluorinated under similar conditions. The fluorination of N₂O over dry powdered CsF was carried out in hopes of synthesizing new N, F, O compounds. The vapor pressure of N₂O over CsF showed no deviation from N₂O itself over the temperature range over which N₂O exists as a liquid. The acidity of N₂O is apparently insufficient to form a CsF complex. Fluorination of the N₂O-CsF mixture at -80°C for 5 days resulted in no reaction.

Cesium Fluoride-Chlorine Monoxide Complex Studies

The alkali metal complexes of Cl₂O and Br₂O represent a new class of compounds. The stoichiometry and structure of these compounds are of interest not only because of their unique nature but also because they may provide an insight into the paths leading to the formation of oxyhalogen fluorides upon fluorination. An investigation of the cesium fluoride-chlorine monoxide system was undertaken to determine the stoichiometry and stability of complexes. The ratio of Cl₂O to CsF was found to be variable, decreasing with increased temperature, pumping, and duration of the experiments. Moreover, the ratios were not reproducible. Large excesses of Cl₂O were held over CsF at -80°C for 17 days and longer and then pumped overnight to remove uncomplexed Cl₂O. The resultant ratios were 1.52, 0.82, and 0.25 during three separate experiments under these conditions and point out the nonreproducible surface conditions and degree of contact during formation of Cl₂O-CsF complexes. The pressure of Cl₂O above such complexes was less than 4 mm at -23°C.

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Investigation of Possible Mercury Hypochlorite Formation

In the course of preparing Cl_2O from yellow HgO and Cl_2 , it was observed that at ~80 C there was some complexing between the generated Cl_2O and the residual mercury salts. To determine if this complexing is caused by HgCl_2 or hypochlorite formation, several experiments were conducted on the possible reaction of HgCl_2 and Cl_2O at ~80 C. The initial experiment indicated that there was some complexing and furthermore that the Cl_2O was converted partially to Cl_2 . Additional effort and experiments failed to duplicate this first result and showed no complexing or reaction between these materials. Therefore, the observed complexing of Cl_2O in its synthesis from HgO remains unexplained.

X-ray powder analysis of the solid product formed by reaction of HgO with excess Cl_2 showed only lines corresponding to HgCl_2 . Although the possibility of amorphous or isomorphous mercury hypochlorite exists, apparently the only important reaction with excess chlorine is:



The unusual behavior of the solid product (i.e., turning brown and evolution of chlorine) may be attributed to complexes with Cl_2 or Cl_2O , or amounts of products other than HgCl_2 too small to be observed by simple X-ray powder analysis.

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EXPERIMENTAL EFFORT

PREPARATION OF Cl₂O

The details of the new static method for preparing Cl₂O have been presented previously (Ref. 2). With the earlier dynamic method it was necessary to use freshly prepared yellow HgO. During this period, however, it was determined that the static method is efficient enough to permit the use of commercial yellow HgO. While the yields of Cl₂O are not quite as high as those achieved with the fresh HgO, they are nevertheless quite good; i.e., 90- to 97-percent Cl₂O using either 1:1 or 2:1 HgO to Cl₂ mole ratios. This compares to 95+ percent with fresh HgO. Using the flow technique, the commercial material produces only a 20- to 25-percent conversion of the Cl₂ to Cl₂O. Therefore, if desired, the preparation of fresh HgO may be avoided with only minimal loss of efficiency in the conversion using the static technique.

PREPARATION OF KrF₂

Krypton difluoride was prepared by circulating an approximately 1:1 molar mixture of Kr and F₂ through an electric discharge reactor cooled to -196 C. The apparatus and technique are nearly the same as that reported in the literature (Ref. 5). Changing the temperature of the discharge tube to -80 C resulted in no reaction.

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency Washington 25, D.C.	
13 ABSTRACT The fluorination of KF and CsF complexes of Cl ₂ O has yielded ClF ₃ O. Thermal dissociation of KClF ₄ O occurred below ambient temperature while heating was required to dissociate CsClF ₄ O. Oxychlorine trifluoride has also been prepared from chlorine nitrate in a 95+ percent yield by fluorination of the complex CsClFONO ₂ . The reaction was independent of the presence of N ₂ O ₄ . Glow discharge experiments at -196 C with solid Cl ₂ O and activated fluorine gas have resulted in small quantities of ClF ₃ O, but ClF ₅ and FC1O ₂ were the major products. The hydrolysis of ClF ₅ with potassium fluoride dihydrate and excess potassium fluoride was carried out in a flow system. No ClF ₃ O was obtained. The ratio of CsF to ClF ₃ O in this complex has been determined to be 1.15 when using excess ClF ₃ O. Experiments with excess CsF also demonstrated an incomplete attainment of stoichiometry, indicating unfavorable kinetics for the reaction. Reversible dissociation of the complex occurs below 150 C. Oxychlorine trifluoride was displaced from its CsF complex by ClF ₃ and from its PF ₅ complex with FNO. Vapor pressure/temperature equations for the ClF ₃ O·FNO and (ClF ₃ O) ₂ SiF ₄ complexes were obtained. The synthesis of ClF ₃ O was attempted by the fluorination of CsClF ₄ O and by the reaction of KrF ₂ with ClF ₃ O. Partial fluorination of Cl ₂ O·CsF was investigated as a route to chlorosyl fluoride and gave only traces of an unidentified substance thought to be FC1O. The reduction of ClF ₃ O as a possible route to FC1O was tried with the reducing agents Cl ₂ O, S ₂ O ₈ ²⁻ , Br ₂ , and BrF ₃ . The complex of Br ₂ O and CsF has been fluorinated in hopes of forming BrF ₃ O or BrF ₅ O. (C)		

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